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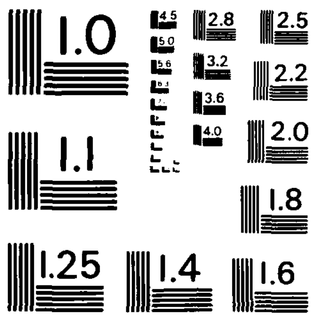

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FINAL TECHNICAL REPORT

STUDY IN MOLECULAR LASERS

by

Professor George Burns

Department of Chemistry

University of Toronto

Inclusive Dates: 1 Novemeber 1980 - 30 April 1984

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A sensitive LIF system was constructed, using a Nd:YAG plus dye laser. The signal was accumulated and analyzed by employing a Tektronix R7912 transient Digitiser and a PDP-11 minicomputer. Reactivity of HF(v=5) was studied. Using the same equipment, a time-delayed photoemission from a trialkali photosensitive semiconductor was observed and results are now being examined.

Using 3-D trajectory calculations a new computational observable, the relative nonequilibrium distribution (RNED) function at the steady state was determined for the Br + Ar reaction at 3500K. It is characterized by one adjustable parameter equal to 12, while the transition state theory prescribes that it should be infinitely large. RNED will be used to test and refine modern theories of reaction kinetics.

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18. Laser-induced chemical reactions.

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The experimental approach to the study of chemical reactions in molecular lasers was centered around a sensitive LIF apparatus in which reactions were generated by a Quanta Ray Nd:YAG plus a dye laser, which was tuned using a photoacoustic detector. Reactivity of HF(v=5) with unsaturated hydrocarbons was studied.[1] Using the same equipment, it was possible to observe a time-delayed multielectron photoemission (TDMP) from a trialkali antimonide photocathode.[2] The initiation of this photoemission is correlated to irradiation of photocathode with a weak (less than 1 femptojoule/cm^2) light pulse which appeared to be statistical. However generation of multielectron pulses from the surface of the photocathode was not statistical with up to 30 electrons leaving the photosensitive surface within the time resolution of the equipment. Such pulses are separated in time during which there are no electrons emitted. The phenomenon is now being studied as a function of light intensity, temperature, and the wavelength of the incident radiation.

A comprehensive review of experimental studies of dissociation recombination reactions was completed.[3]

Diatom dissociation and atomic recombinations, occurring in molecular lasers, were studied using the 3-D trajectory calculations technique, in which over 10^5 trajectories were generated.[4] The single uniform ensemble method previously employed in 3D classical trajectory calculations (H. D. Kutz and G. Burns, J. Chem. Phys. 72, 3652 (1980) was used. It was applied to the Br_2 + Ar system to study nonequilibrium effects in diatom dissociation over a wide temperature range. It was found that, for a given large set of trajectories, observables, such as reaction cross sections or rate constants, are independent within four significant figures of the initial distribution function. This indicates a high degree of reliability of the single uniform ensemble method, once the choice of a set of trajectories is made. In order to study dissociation from the low lying energy states, the uniform velocity selection method in trajectory calculations was used. It was found that dissociation from these states contributes but little to the overall dissociation reaction. The latter finding is consistent with the attractive nature of the potential energy surface used, and constitutes an argument against those current theories of diatom dissociation reaction which explains experimental data by postulating a high probability of dissociation from low lying energy states of diatoms. It was found that the contribution from the low lying states to dissociation can be estimated with good accuracy using information theory expressions. Temperature dependence of nonequilibrium effects was investigated between 1 500 and 6 000°K. In this range the nonequilibrium correction factor varies between 0.2 and 0.5. Angular momentum dependence of such observables as reaction rate constant and reaction cross section was investigated.

It was possible to define a new computational reaction kinetic "observable," $d^{ss}(E)$, the relative nonequilibrium energy distribution (RNED) function at the steady state.[5] The

$d^{ss}(E)$ is a plot of relative molecular densities of diatoms vs. their internal energies. The RNED, obtained as a histogram, proved to be significant for several reasons, one of which was that it can be described with a remarkably high degree of precision by a simple algebraic function. The latter is calculated from known constants and physically meaningful constraints. It required only one adjustable parameter, $\underline{a}$. For the case of Br_2 dissociating in Ar at 3 500°K, $\underline{a} = 12.0 \pm 0.3$, which is intriguing because the transition state theory prescribes $\underline{a} = +\infty$ for all reactions. The study of d(E) and of $\underline{a}$ might provide a novel method for testing the transition state and other quasi-equilibrium theories. Preliminary results indicate that the much used strong collision assumption of unimolecular reaction theories is inadequate in describing reactions occurring on strongly attractive surfaces.[6] Much work on this project is now being prepared for publication.

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